Evidence for a transition from a bulk Meissner-state to a spontaneous vortex phase in $RuSr_2GdCu_2O_8$ from DC magnetisation measurements

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Abstract

From magnetisation measurements we provide evidence that the ferromagnetic superconductor $RuSr_2GdCu_2O_8$ with T_c=45 K and T_M=137 K exhibits a sizeable diamagnetic signal at low temperature ($T<T^{ms}$=30 K) and low magnetic field (H^{ext}<30 Oe), corresponding to a bulk Meissner-phase. At intermediate temperatures, $T^{ms}<T<T_c$, a spontaneous vortex phase forms which is characterized by unique thermal hysteresis effects. We argue that a recent negative report [C.W. Chu et al., cond-mat/9910056] regarding the Meissner-effect in Ru-1212 can be explained by impurity scattering or grain size effects.

Superconductivity (SC) and ferromagnetism (FM) are two antagonistic phenomena. The question as to whether both order parameters (OP) can coexist on a microscopic scale has attracted a great deal of ongoing interest. Experimentally, a coexistence of SC and long-range FM order was first discovered in 1976 in the ternary rare-earth compounds $ErRh_4B_4$ [1] and $HoMo_6S_8$ [2]. In these materials the SC state forms at higher temperature (T_c<10 K) than the FM state (T_M<1 K), however, both temperatures are rather low. The formation of the FM state eventually leads to the destruction of SC (reentrant behavior). Albeit, there exists a narrow intermediate temperature range where both SC and FM order can coexist. In this intermediate state the FM order exhibits a spiral modulation or a domain-like structure (depending on the magnetic anisotropy of the system). The modulation of the FM OP helps to circumvent the detrimental pairing-breaking effect due to the exchange interaction (EXI), which prevents singlet pairing (but not triplet pairing) by lifting the degeneracy of the spin-up and spin-down electrons of a Cooper-pair, and the electromagnetic interaction (EMI), which induces screening currents that suppress SC once the internal fields exceed the upper critical field H_{c2} [3]. Likewise also the SC OP may be spatially modulated as realized in a spontaneous vortex phase (in response to the EMI) or in a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) phase [5] (in response to the EXI).

Renewed interest in the interplay between FM and SC order has been stimulated by the recent discovery of coexistence of FM and SC order in the ruthenate-cuprate compound $RuSr_2GdCu_2O_8$ (Ru-1212) [6–8] (and possibly also in $RuSr_2(Gd,Ce)_2Cu_2O_{10}$ (Ru-1222) [6,9]). In these materials the FM transition occurs at a considerably higher temperature than the SC one, i.e., in Ru-1212 T_M=132-138 K and $T_c \approx$45 K. Rather surprisingly, it was found that the onset of SC does not induce any significant modification of the FM order [8]. On the other hand, it is still an open question as to how the SC OP, which is thought to originate in the CuO_2 bilayers, is modified in the presence of the already developed FM OP, which involves the moments in the Ru-O layers. Recent proposals include the possibility of a FFLO-type state [10] or of a spontaneous vortex phase (SVP) [10,11,9]. Obviously, these new materials with their novel and extraordinary properties promise to be unique model

systems for studying the complex interplay of SC and FM order.

First of all, however, one has to worry about the chemical and structural homogeneity of these complex materials. One is confronted with three major concerns: 1) are the FM and the SC phases intrinsic to the Ru-1212 compound, or is one of them related to a minor impurity phase; 2) does the FM OP persist throughout the entire volume of the sample; and 3) is the same true for the SC OP? Already there exists ample evidence that the answer to the first two questions is positive. High-resolution synchrotron X-ray diffraction [12] and neutron diffraction measurements [13,14] indicate a high structural and chemical homogeneity of our Ru-1212 samples with no detectable impurity phases. Secondly, muon-spin rotation (μSR) measurements [8] and later electron-spin resonance (ESR) measurements [15] have shown that the FM order is a uniform bulk effect. The remaining unresolved third question thus concerns the homogeneity of the SC phase. Evidence in favor of a bulk SC state has been obtained for Ru-1212 from specific heat measurements where a sizeable peak in the specific heat coefficient γ was observed at T_c, comparable to that for non-magnetic underdoped Y-123 or Bi-2212 cuprates with a similar T_c ~40-50 K [16]. On the other hand, Chu and coworkers recently casted doubts as to whether Ru-1212 is a bulk SC [11]. They find that a bulk Meissner-effect, generally considered as the key indicator for bulk SC, does not exist in Ru-1212. They argue that the SC signal might be due to an impurity phase which is not even detectable by X-ray or neutron diffraction experiments. Alternatively, they suggest that the absence of a Meissner-effect could be attributed to the creation of a SVP. Such a SVP can be expected to form in a FM superconductor if the spontaneous magnetisation, $4\pi M$, exceeds the lower critical field H_{c1} (as defined in the absence of the spontaneous magnetisation), i.e., if $4\pi M > H_{c1}(T{=}0)$. [4,10,11] Otherwise, if $H_{c1}(T{=}0) > 4\pi M$, the Meissner-state will be stable at low temperature. Moreover, since $4\pi M$ is only weakly T-dependent below $T_c \ll T_M$ while H_{c1}(T) falls to zero at T_c, a transition to an intermediate SVP will occur at the temperature T^{ms} where $H_{c1}(T^{ms}) = 4\pi M$.

In this Letter we present low-field dc magnetisation measurements on polycrystalline Ru-1212 samples, which provide evidence that a bulk Meissner-state develops in the pure

compound at low temperature, with $T^{ms} \leq 30$ K varying from sample to sample. In addition, we show that the SVP, which forms at intermediate temperatures $T^{ms} < T < T_c$, is characterized by unique thermal hysteresis effects. We argue that the absence of a Meissner-phase in Ru-1212 as reported by Chu et al. [11] can be explained in terms of a moderate reduction of H_{c1} due to impurity scattering or grain size effects.

Two polycrystalline, pure (SC) $RuSr_2GdCu_2O_8$ samples (**A** and **B**), and one Zn-substituted (non-SC) $RuSr_2GdCu_{2.94}Zn_{0.06}O_8$ sample (**C**) have been prepared as described previously [7,8]. The duration and the temperature of the final sintering step have been slightly varied: 96 h at 1060 °C in flowing O_2 for **A** and **C**; and 20 h at 1055 °C for **B**. It was previously shown that prolonged sintering at 1060 °C helps to remove 90° [100] rotation twins and also a minor degree of intermixing of Ru↔Cu and Sr↔Gd [7,8]. Apart from these differences, high-resolution X-ray diffraction (XRD) [12] and neutron diffraction measurements [13,14] have confirmed that our samples contain no impurity phases above the limits of sensitivity (∼1%). The electronic properties have been characterized by resistivity and thermo-electric power (TEP) measurements. The onset of the drop in resistivity and the temperature where the TEP becomes zero indicate T_c =45 K for samples **A** and **B** and T_c<4 K for the Zn-substituted sample **C**. [7,8,16] All samples have been further investigated by μSR measurements which confirm that the FM ordering of the Ru-moments and also the antiferromagnetic (AF) ordering of the Gd-moments is hardly affected by the thermal treatment or by Zn-substitution [17]. The DC magnetisation measurements have been performed with a Quantum Design MPMS7 magnetometer.

Figure 1 shows the volume susceptibility, χ_V, of samples **A** and **C** obtained after zero-field cooling (zfc) to 2 K before applying an external field $H^{ext} = 6.5$ Oe. A value of ∼95% of the ideal density $\rho = 6.7$ g/cm^3 of stoichiometric $RuSr_2GdCu_2O_8$ with $a = 3.84$ Å and $c = 11.57$ Å [7,12] has been determined for samples **A** and **C** and was used to calculate the susceptibility. We have not corrected for the demagnetization factor which should be small since the samples have a bar-shaped form and H^{ext} is parallel to the long axis. The FM ordering of the Ru-moments is marked for both samples by a cusp in χ_V at T_M=137

(**A**) and 132 K (**C**). In sample **C,** χ_V exhibits a pronounced increase below 50 K due to the paramagnetic contribution of the Gd-moments which order antiferromagnetically (AF) at 2.5 K (as indicated by a cusp in χ_V and as seen in μSR [8,17] and neutron diffraction [14]). For the SC sample A, however, a sizeable diamagnetic shift occurs at T^{ms} = 30 K. This is not the thermodynamic SC transition, which occurs at $T_c \approx$45 K [16] and is marked by a weak diamagnetic shift as shown in the enlargement in the inset to Fig. 1.

Figures 2 shows the field-cooled (fc) volume susceptibility, χ_V, of sample **A** (solid lines) at 0.5$\leq H_{ext} \leq$500 Oe and of sample **C** (dotted lines) at 0.5, 2.5 and 100 Oe. The external field was changed at 200 K with the sample in the paramagnetic state. The low fields were measured by a comparison of the respective paramagnetic signals at 200 K with the signals measured at 50$\leq H_{ext} \leq$500 Oe. For both samples a spontaneous magnetisation develops at similar temperatures of T_M=137 K (**A**) and T_M=132 K (**C**) and below $\sim$100 K it rises almost linearly with decreasing temperature. A clear difference appears only below 30 K where the susceptibility of the SC sample is strongly reduced as compared to the Zn-substituted one. For the Zn-substituted sample χ_V increases rather steeply at low T due to the paramagnetic contribution of the Gd-moments. In marked contrast, for the SC sample χ_V decreases suddenly below T^{ms}=30 K (corresponding to a sizeable diamagnetic shielding) and remains almost T-independent below T^{ms}. Evidently, in the SC sample the paramagnetic Gd-moments are screened against the external field and also the internal spontaneous magnetisation. In other words, the SC sample is in a bulk Meissner state at $T<T^{ms}$. Apparently, the paramagnetic Gd-moments provide a very useful probe for the Meissner-effect. Below we argue that the observed behavior is indicative of a transition from a Meissner-phase at $T<T^{ms}$=30 K to a SVP at T^{ms}=30 K$<T<T_c$=45 K. The volume fraction of the Meissner-phase as estimated from the size of the diamagnetic shift, $(\chi_V(T \rightarrow 0) - \chi_V(T^{ms}))/(\chi_V(T^{ms})+1)$, is shown in the inset of Fig. 2(b) as a function of H^{ext}. Apparently the Meissner-fraction is almost 40 % at 0.5 Oe but falls very steeply as a function of H^{ext}. Our estimate gives only a lower limit for the Meissner-fraction. The diamagnetic shielding tends to be reduced by vortex pinning and also by the small average grain size of around

2-10 μm (which is further reduced due to 90° [100] rotation twins and antiphase boundaries) which is almost comparable to the magnetic penetration depth λ. Assuming an average grain radius r=3 μm and an effective magnetic penetration depth $\lambda_{eff} = \sqrt[3]{\lambda_{ab}^2\lambda_c}$ ~500 nm, we obtain from the Shoenberg-formula $\chi/\chi_o = 1 - (3\lambda/r)\coth(r/\lambda) + 3\lambda^2/r^2 \approx 0.5$ [18], i.e. a two times larger Meissner-fraction. Note that λ_{eff} ≈500 nm is quite a reasonable assumption since the unique dependence of T_c on λ in underdoped cuprate SC [19] implies λ_{ab} ≈300 nm for T_c ≈45 K, whereas λ_c typically exceeds 2000 nm [18]. Based on these considerations we conclude that sample **A** exhibits a bulk Meissner-state with the volume fraction exceeding 40 %.

This brings us to the interesting question as to why no evidence of a bulk Meissner-phase has been obtained in a recent study on seemingly similar Ru-1212 samples [11]. A straightforward explanation is that $H_{c1}(T{=}0)$ is moderately reduced in these samples. As was noted above, if $H_{c1}(T = 0) < 4\pi M$, a SVP will be energetically more favorable than the Meissner-phase even at zero applied field and at zero temperature. H_{c1} may be reduced by pair-breaking due to magnetic (or non-magnetic) defects causing a reduction of the SC condensate density and a commensurate enhancement of λ (which is particularly strong in case of a SC OP with d-wave symmetry [20]). We speculate that such defects may arise, for example, due to some intermixing between Cu and Ru or to antiphase boundaries in the rotation pattern of the RuO_6 octahedra such as observed by x-ray and neutron diffraction [7,12,13]. Also, since the effective value of H_{c1} depends on the ratio of λ/r, the morphology of a given Ru-1212 sample (for example the amount of [100] rotation-twins [7]) may actually determine whether or not it exhibits a Meissner-effect. The data in Fig. 2 imply that H_{c1}(T=0) in our sample **A** exceeds $4\pi M$ by less than 30 Oe since the diamagnetic shift at T^{ms} diminishes very rapidly as H^{ext} increases. At 35 Oe the susceptibility already starts to exhibit a slight paramagnetic T-dependence due to the Gd-moments that are no longer screened against the local fields. From the remanent magnetisation found after high field saturation measurements [8] we estimate that $4\pi M$ is of the order of 50-70 Oe. Note that 4πM is about 10 times smaller than the internal field of ~700 Oe as obtained from μSR measurements

[8] or deduced for the case that the Ru-moments of size $1\mu_B$ exhibit purely ferromagnetic order. This difference may indicate that the Ru-moments exhibit a canted antiferromagnetic order with only a $\sim$10 % ferromagnetic component. Under the assumption that $4\pi M$ is only weakly T-dependent below $T_c << T_M$ and using $H_{c1}(T^{ms})=H_{c1}(\mathrm{T}=0)\times(1-(T^{ms}/T_c)^2)=4\pi M$ with T^{ms}/T_c=30/45, we then obtain H_{c1}(T=0) of the order of 80-120 Oe. In turn this gives $\lambda = \sqrt{\Phi_o/H_{c1}}$ $\sim$400-500 nm in reasonable agreement with our above estimates.

The finding that T^{ms} appears to decrease only slightly from 30 K at 0.5 Oe to 27 K at 10 Oe can be understood due to the random orientation of the spontaneous magnetisation of the individual FM domains with respect to the external magnetic field. For very small external fields the domains will not be aligned and in most domains the effective internal field will be only marginally increased or even be decreased. However, once these domains become aligned by a sufficiently large field H^{ext}, the internal field will suddenly be increased to a value $4\pi M + H^{ext} > H_{c1}(T=0)$. For the individual domains the alignment thus will trigger a sudden transition from a state with a Meissner-phase below $T^{ms} \simeq 30$ K to one where the SVP persists to the lowest temperatures.

In the following we show that the transition temperature of the Meissner-phase T^{ms} varies considerably even among samples that have been prepared under similar conditions. Figure 3 shows the fc data at 6.5 Oe for sample **B** which has been sintered at slightly lower temperature and for a shorter period as described above. Sample **B** has the same critical temperature $T_c = 45K$ as sample **A** (as confirmed by transport and thermodynamic measurements [7,16]), but a Meissner-phase forms only at significantly lower temperature $T^{ms} \approx$16 K. Another interesting feature is the strong thermal hysteresis of χ_V at the transition from the vortex phase to the Meissner phase. Upon cooling (solid line) the transition occurs at a distinctively lower temperature (of about 1 K) than upon warming (dotted line). Notably, the hysteresis occurs only after the sample has been cooled below T^{ms}. It is absent if the sample is only cooled to T=17 K (crosses) and subsequently warmed (open circles). This kind of hysteresis, in particular the undercooling effect, is indicative of a first-order transition such as from a SVP to a Meissner-state where the magnetisation exhibits a dis-

continuous change. In the SVP flux-lines are formed which penetrate the sample volume completely. Below T^{ms}, as the Meissner-state develops, the flux-lines are expelled from the interior of the grains. However, pinning of the vortices by any kind of defects will lead to an incomplete expulsion of the vortices and thus will reduce the diamagnetic shift. On warming the sample again above T^{ms}, the flux-lines have to reenter the individual grains. Pinning will hinder the vortices from reentering the superconducting grains. This leads to hysteresis as shown in Fig. 3, where the magnetisation upon cooling is higher than that upon subsequent warming.

In sample **A** the signature of the hysteretic transition at T^{ms} is less pronounced, probably because it contains fewer defects that act as pinning centers and its transition temperature, T^{ms}=30 K, is almost twice as high. However, yet another kind of thermal hysteresis related to the magnetisation of the Gd-moments occurs for H^{ext} $\geq$35 Oe, once the SVP persists to low T. As noted above, the paramagnetic Gd-moments eventually become partially aligned in the local field at low T and therefore give rise to a sizeable enhancement of the spontaneous magnetisation. Note, that in the SVP the density of the vortices is not only determined by H^{ext} but, in addition, by the spontaneous magnetisation. Therefore, even though H^{ext} is constant for a fc curve, the vortex density tends to increase upon decreasing the temperature as the Gd-moments become aligned by the local field. Any vortex pinning thus will lead to thermal hysteresis such as shown in Fig. 4 where χ_V is lower upon cooling (solid lines) than upon warming (dotted lines). We have confirmed that such hysteretic behavior of the magnetisation does not occur for the Zn-substituted (non-SC) sample C (not shown here). The observed unique hysteretic behavior therefore gives yet another demonstration of the direct interaction between SC and FM order in the SVP and thus of their microscopic coexistence.

In summary, we have presented dc magnetisation measurements which provide evidence that the FM superconductor $RuSr_2GdCu_2O_8$ develops a bulk Meissner-state. In addition, we show that the spontaneous vortex phase forming at intermediate temperature, $T^{ms} < T < T_c$, is characterized by unique thermal hysteresis effects. We outline that the absence of a

Meissner-phase in Ru-1212 as reported by Chu et al. [11] can be explained in terms of a moderate reduction of H_{c1} due to impurity scattering or grain size effects.

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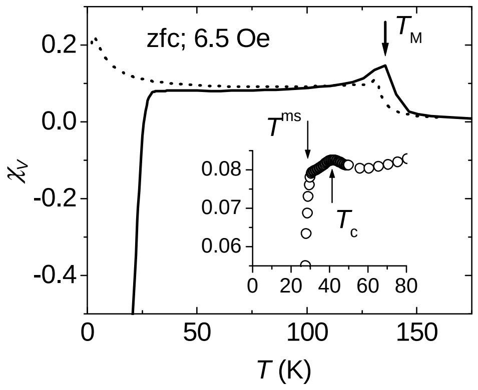
I. FIGURE CAPTIONS

Figure 1: Zero-field-cooled (zfc) volume susceptibility, $\chi_{V,}$ at 6.5 Oe of the pure sample **A** (solid line) and the Zn-substituted sample **C** (dotted line). Inset: Susceptibility of sample **A** around the SC transition, $T_c = 45$ K, shown on an enlarged scale.

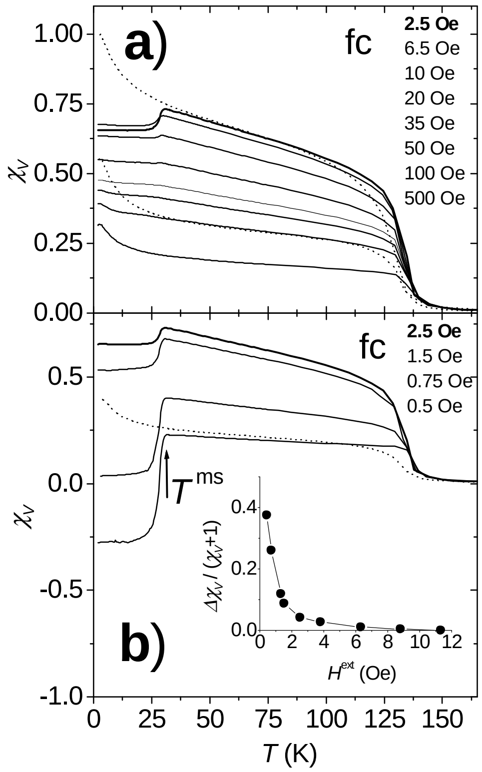
Figure 2: Field-cooled (fc) volume susceptibility, χ_V, (a) of the pure sample **A** at 2.5, 6.5, 10, 20, 35, 50, 100 and 500 Oe (solid lines) and the Zn-substituted sample **C** at 2.5 and 100 Oe (dotted lines); (b) of sample **A** at 2.5, 1.5, 0.75 and 0.5 Oe (solid lines) and sample **C** at 0.5 Oe (dotted line).

Figure 3: Low temperature fc curve at 6.5 Oe for the pure sample **B** which has the same $T_c = 45K$ as sample **A** but has been prepared under slightly different conditions as noted in the text. The Meissner-phase forms at significantly lower temperature T^{ms} ≈16 K. Note the thermal hysteresis of χ_V around T^{ms} which is absent if the sample is only cooled to T=17 K (crosses) and subsequently warmed (open circles).

Figure 4: Thermal hysteresis of the fc data of sample **A** at 35, 50, 100, 250 and 500 Oe. The solid lines (dotted lines) show χ_V upon cooling (warming). Arrows indicate the direction of the temperature change. At 100 Oe two hysteresis curves for cooling to 2 and 4 K are shown by the thick and thin dotted lines, respectively.



Bernhard et al., Fig. 1



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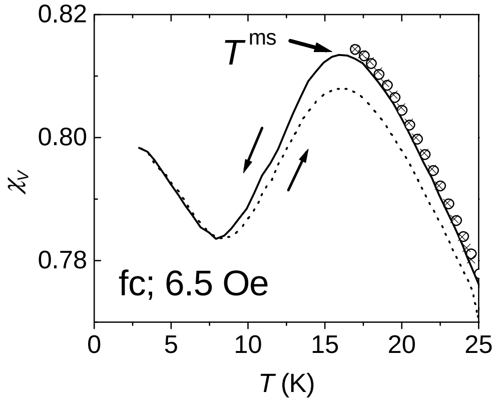

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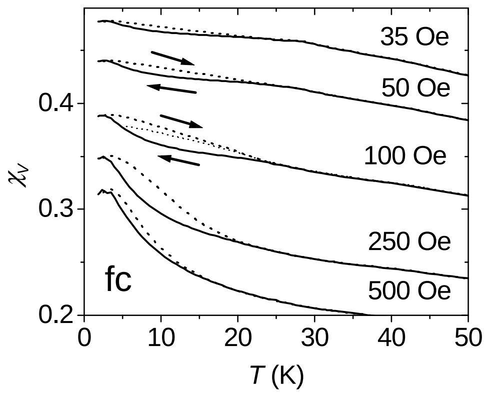

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